MIM/Ceramic Part Debinding Methods

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The variety of binders and lubricants used in manufacturing powder metal and ceramic parts present various problems when they need to be removed during part processing. Several techniques have been developed to efficiently handle this step in the manufacturing process.

Vaccum/controlled-atmosphere furnace design typically requires the use of metal radiation shields or graphite insulation, which precludes the use of oxygen atmospheres during debinding because it will damage the hot zone. On the other hand, with some oxide and nitride ceramics, such as alumina, zirconia and aluminum nitride, common refractory-lined oxygen furnaces are used to thermally combust the binder. In the presence of air, carbonaceous binders burn readily and more completely than they would in a blanket of inert gas. Unfortunately, most metals and nonoxide ceramics react with oxygen even at the lower temperatures at which the debinding process is carried out, forming oxide coatings, which are difficult to remove later during sintering.

Binders and lubricants commonly used in metals and ceramics processing are shown in Table 1.

Injectavac™ process for MIM

The Injectavac process, pioneered by Centorr/Vacuum Industries in the early 1980s, was one of the first integrated debind and sinter processes for the metal-injection-molding (MIM) industry. Early research by Kennedy and Finn documented the problems in removing the large quantities of binders found in MIM feedstocks[1]. The most common formulation consisted of a paraffin wax first stage, a polymer second stage and surfactant surface agent. The large quantities of wax in MIM compacts were too much for the Sweepgas condenser trap. Improved gas-flow dynamics also was required to sweep away the large volume of binder. Gas flow up to 25 times greater than that of the hot zone volume per hour can be required for effective binder removal.

The second-stage polymer also was equally difficult to handle, as the material did not behave like a wax (which condenses back to its original state). The high molecular weight polymer has a high vapor pressure, making the vacuum level inconsequential. The thermally decomposed polymer breaks down into CO, CO_2 and low molecular weight hydrocarbon gases, which form small diameter smoke-like particles. This material was difficult to trap in conventional cold traps, which led to the development of the Injectavac BRS (binder removal system) process.

Metal hot zone in MIM sintering furnace

Table 1 Binders/lubricants used in metal/ceramic powder processing

Process	Binders/lubricants
Powder metallurgy	Acrawax,C, zinc and lithium stearates
Powder metal/ceramic injection molding	Paraffin wax, polyethylene (PE), polypropylene (PP), polyacetal (PA), agar and water-soluble polyvinyl alcohol
Ceramic processes	Methylcellulose, phenolics, polyvinyl acetate, acrylics, caoutchouc glue, methyl methacralate and colloidal silica

Figure 1 shows a typical Injectavac furnace cycle.

The hot zone in an Injectavac furnace incorporates a graphite retort design and modified sweepgas system similar to that used in tungsten-carbide vacuum dewax. The difference is the incorporation of a pump-out tube in the bottom of the retort penetrating the hot zone, allowing the evaporated wax to be removed to the chamber annulus without having to pass through the hot zone insulation or elements. The sweepgas also is plumbed directly into a box plenum at the rear of the retort (not into the chamber), and is only used during second-stage polymer removal, not during wax removal. The plenum preheats the gases and ensures consistent gas flow over all the trays in the workload.

To remove the large volume

of wax (up to 30 to 40 vol%), a diffusion pumping system is included, which has a large diameter port to achieve vacuum levels down to 10^{-3} to 10^{-4} torr during debinding. This allows fast evacuation of the paraffin wax at lower temperatures. No modulating valve or vacuum sensors are used to control vacuum levels. The pump simply is allowed to pump to its best vacuum level. As the wax passes through the diffusion pumping system, the "jetting" oil particles knock down the wax vapor, forcing it through the heated foreline manifold and on to the binder removal pump. While the wax does not contaminate the diffusion pump or its oil, some users prefer simply to use a mechanical OTO (once-through oiling) pump during the wax removal stage, and only use the diffusion pump during sintering if required. Figure 2 shows the effect of vacuum level on debinding time.

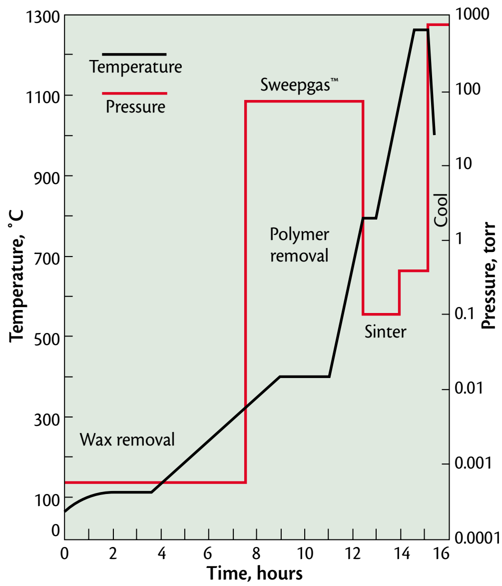

Fig 1 Typical binder removal and sintering cycle for an Injectavac furnace

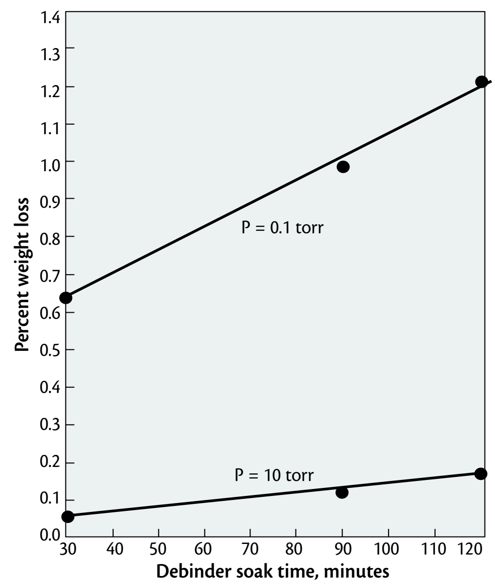

Fig 2 Effect of pressure on binder removal times.

As with the vacuum dewax process, the chamber is plumbed with both hot and cold water to allow the jacket to be heated above the wax-melting temperature, and the chamber is pitched on a 3° tilt allowing the wax that collects on the walls and bottom of the chamber to pour into a manually valved wax reservoir pot with spigot.

The heart of the system is the specially designed mechanical pump/blower combination for wax/polymer binder removal. It consists of a BRS™ once-through oiling pump, which continuously supplies fresh, clean oil to the compression chambers rather than recirculating oil from a sump. The oil (SAE 40 nondetergent-grade motor oil) does not remain in the pump long enough for the contamination to be a problem. After passing through the pump, the oil is discharged to a collection container. The binders/polymers that normally would contaminate the oil (or build up in the pump) pass through with the oil and are continuously discharged. In addition, the oiling technique enhances bearing and seal lubrication for long trouble-free pump operation.

Critical second stage polymer binder removal is accomplished using a traditional Sweepgas technique. Inert gas is bled into the furnace chamber and enters the work box where it entrains polymers vaporized from the workpieces. The vapors are carried out toward the BRS system, which pumps them directly through to the collection system while maintaining a quality operation. The simplicity of the system is that there are no traps to clog and no filters to clean or replace. The thoroughness of the binder removal allows the successful processing of stainless steels such as 316L and 17-4PH. This combined with the lower initial investment of a graphite furnace and lower operating and maintenance costs is an advantage. The Injectavac process for debinding MIM parts is shown in Fig. 3.

Sweepgas™ for MIM

Metal hot-zone designs for processing MIM components gained in popularity in the industry due to tight MIM-processing windows and a demand for higher cleanliness levels. Because of the expense and brittle nature of molybdenum and tungsten refractory metals used in construction, most manufacturers prefer to carry out first stage debinding in separate low-temperature ovens. Second-stage polymer debinding and final sintering are then carried out in vacuum sintering furnaces. Even with the advent of solvent debinding, the long debind cycle times required make it wise to carry out this process in lower cost units instead of tying up valuable time in expensive sintering furnaces.

This version of sweepgas processing has a number of improvements designed specifically for use with MIM feedstocks. Tight partial pressure control and consistent gas flow with sound retort design allows the entire load to see the same series of conditions as a function of time. This results in consistent microstructures and repeatable carbon control. The gas-plenum retort has rows of perforations allowing even gas flow across all the work trays. Alumina ceramic support members are used for ease of construction and replacement.

Unlike traditional Sweepgas for hardmetals, which is designed to operate at a maximum partial pressure ranging from 0 to 10 torr, MIM Sweepgas (using either inert or hydrogen process gas) must operate in a partial pressure ranging from 1 to 500 torr. Instead of flowing the sweepgas into the chamber and letting it diffuse through the hot zone into the retort, the MIM gas circuit plumbs gas to both the outside of the chamber and the gas plenum retort. The MIM Sweepgas process for debinding is shown in Fig. 4.

The retort gas flows over the trays to sweep away binder off-gasses, while the chamber "guard" gas ensures minimal binder condensation on the cold chamber walls. The binder-laden gas is pumped out the bottom of the retort through a pump-out tube. A closed-loop controller receives a pressure-signal input from the retort capacitance manometers, and the output automatically adjusts an electromechanical modulating valve to regulate pumping speed and provide constant pressure control within the retort during debinding. This is critical as large swings in vacuum level during debinding can have catastrophic consequences. Excessive sweepgas flow during polymer removal also can cause a problem as the gas can blow apart fragile parts spraying metal powder over the inside of the hot zone where it is later sintered.

Sintering using a partial pressure hydrogen atmosphere is relatively new process in the MIM industry. While this is in the flammable range of hydrogen (from 15 torr - 75% hydrogen), the environment offers advantages to MIM companies:

- A low partial-pressure reducing atmosphere tends to remove the oxide phase much faster than at positive pressures.
- Less hydrogen gas is used at partial pressures than at positive pressures.
- Small percentages of hydrogen provide a stable reducing environment in case of slight furnace leaks.
- Partial pressures provide a more thorough sweeping action to remove carbonaceous binder byproducts and remove off-gases from the hot zone instead of relying on positive pressure gases to purge them out.
- At partial pressures, any hydrogen that reacts with oxygen to form water vapor is removed by the vacuum pumping system. There also is less hydrogen present to react with graphite hot zones (forming methane, CH_4, gas), which shortens hot zone life and can alter the carbon content of the parts.

The following safety measures are required for systems designed to operate in hydrogen partial pressures:

- Programmable, automatic leak-check cycle
- Pneumatic clamps on front and rear doors.
- Inert gas purge connected to pump gas ballast and inlet and exhaust ports
- Double O-rings on door flanges and binder flanged pots having pumpable grooves.
- Double O-rings on binder pots/traps having pumpable grooves or mechanical locking clamps
- Control logic and all valving in accordance with NFPA 86D regulations

A variety of wax and polymer condensation strategies have been developed to handle different process requirements and feedstock design. The most popular is a T/P (trap over pot) design. It consists of a multistage wax/polymer condenser having removable media baskets filled with high surface area pall rings and stainless steel wool connected to the debind manifold, which is heat traced and insulated to the chamber. The trap body can be outfitted with heater bands and an insulation jacket to allow the canister to self-strip by heating up to the melting point of the wax/polymer, allowing it to melt and flow down into a knockout pot underneath. Depending on the binder system used, the T/P condenser also can be water traced/jacketed to maximize condensation of polypropylene/polyethylene vapors for efficient trapping.

Positive-pressure flow-through debinding

Binders that have high vapor pressures do not lend themselves to vacuum debinding; their high vapor presures make the use of vacuum ineffective, or they decompose into tarry, sticky phases that would quickly destroy vacuum pumping systems. A positive pressure environment is desirable in this case. The primary advantage of positive pressure systems over vacuum debinding is the ability to bathe the part in warm gas, which provides more uniform heating than radiation in a vacuum environment. This is due to the thermal transfer from gas conduction and convection. For a more detailed discussion of positive pressure flow-through debinding, see "Debinding Options for Hard Metals," September 2001 *IH*.

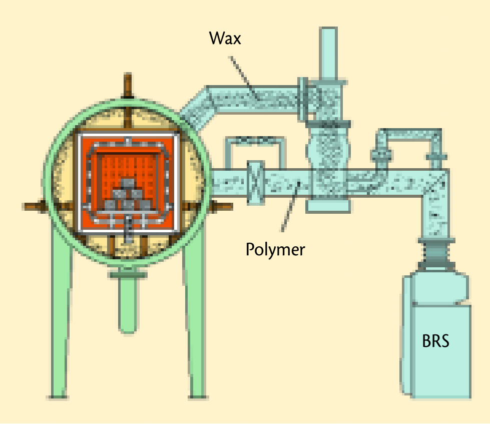

Fig 3 *Schematic of Injectavac process for debinding MIM components*

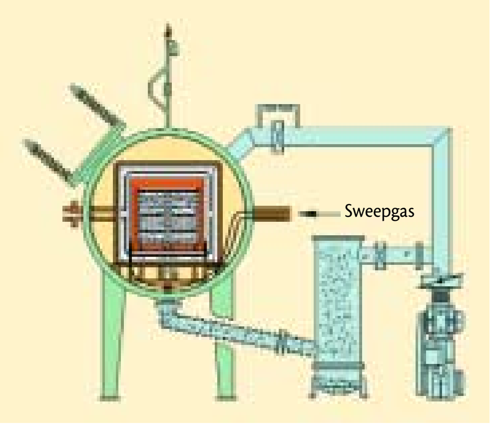

Fig 4 *Schematic of MIM Sweepgas process for debinding MIM parts*

Continuous-furnace debinding

Lubricant removal in hot-wall pusher furnaces and belt furnaces is common in the powder-metallurgy industry. Lubricants are removed in a positive-pressure environment of inert gas or an inert gas/hydrogen mixture. Today's lubricants are designed to burn off cleanly with little leftover residue. However, this is not the case with nonoxide ceramics, tungsten-carbide hardmetals, and MIM parts. More care must be taken during binder removal to ensure that the required residual carbon content is achieved.

An example of the process is illustrated using Centorr Vacuum Industries cold-wall pusher furnace rated for 2300°C (4170°F) operation and having an inline debinding zone. Inert gas is flowed through the back end of the furnace where it cools the parts exiting the sintering zone. The gas sweeps process offgases into the debind zone where the inert gas forces the products of combustion to exit through ports in the bottom of the pusher track to a floor-mounted incinerator. All debind manifolding is insulated to minimize condensation and plugging of the manifolding.

Load locks on both the entrance and exit zones prevent air infiltration (which could affect product quality) and maintain insulation integrity. The graphite pusher furnace can be designed as a vacuum or atmosphere furnace having vacuum debinding or positive-pressure debinding.

Bibliography

1. S. W. Kennedy and C.W.P. Finn, "Metal Injection Molded Part Debinding and Sintering in Vacuum Furnaces," Powder Metallurgy Science and Technology, Vol. 1, No. 3, 1990
2. R. M. German, "Variations in the Essential Powder Injection Molding Processes," Gorham Advanced Materials Institute, Monterrey, Calif., March 1989
3. Fred Andersen, "Performance Evaluation of Gas Atmosphere Delubing and Sintering in Sintervac® Furnaces," Metal Powder Report, February 1984, Vol. 39, No. 2
4. C.W.P. Finn, "Vacuum Binder Removal and Collection," International Journal of Powder Metallurgy, Vol. 27, No. 2, 1991

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